

**Solvent Effects on Surface Composition of Poly(dimethylsiloxane)-co-polystyrene/Polystyrene Blends**

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## Abstract

The effects of mixed solvents used for casting films of diblock copolymer/homopolymer blends of poly(dimethylsiloxane)-co-polystyrene/polystyrene have been studied in detail at the surface of films. The surface composition was determined over a wide range of detection depths using data from various spectroscopic techniques, including X-ray photoelectron spectroscopy (XPS), attenuated total reflection (ATR) FTIR and time-of-flight secondary ion mass spectrometry (ToF SIMS). After surveying a range of solvents, the surface segregation dependence on solvent composition was investigated for two binary solvent mixtures, namely toluene/chloroform and cyclohexanone/chloroform. 100% surface poly(dimethylsiloxane) (PDMS) coverage has been observed for the polymer blends containing 2% PDMS in bulk using the optimized cyclohexanone/chloroform mixture as solvent. Detectable amounts of polystyrene (PS) residue can be observed on surfaces for samples cast from other solvents. The PDMS enriched surface region is much thicker for samples cast from cyclohexanone/chloroform solvent mixtures. ToF SIMS analysis results suggest that casting solvents also alter the surface morphology of sample films. The effect of solvent on the surface composition, depth gradient and surface molecular structure of solution cast films are discussed in terms of polymer-solvent interaction parameters and polarity of solvents.

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## Introduction

The surface properties of poly(dimethylsiloxane) (PDMS) containing polymer blends have been investigated over the last 30 years since the first polymer surface modification using siloxane containing copolymers reported by Zisman and coworkers.<sup>1</sup> A key property of PDMS is its low surface energy, which results in surface segregation of PDMS in most polymer blend systems. This property is often desirable for many applications regarding low surface energy such as antifouling coatings.<sup>2-4</sup> Modification for low energy surfaces can be achieved by blending only a small amount of PDMS containing copolymers into the homopolymer. During solidification of the material, PDMS migrates to the surface of the material, which leaves the bulk phase properties of the material essentially unchanged. The surface properties of modified polymers prepared via surface segregation of PDMS copolymers have been shown to be directly influenced by the structure, molecular weight and the architecture of the copolymer.

The surface segregation of PDMS containing copolymers and copolymer blends has been extensively studied by our group<sup>5-11</sup> and many others.<sup>3, 12-15</sup> Using contact angle measurements<sup>13</sup> and surface tension measurements,<sup>14,15</sup> various groups have reported that as little as 1% of PDMS content in polymer blends could result in almost complete PDMS surface coverage. However, recent investigations, using higher surface sensitive and later quantitative characterization technologies like XPS, have shown that at 1% bulk concentration, the surface is not covered completely with PDMS. A significant amount of homopolymer residue can be detected on sample surfaces.<sup>5,16</sup> Special sample processing techniques have to be used to enhance surface segregation to increase the surface coverage of PDMS.<sup>8,17</sup> Post solution-cast annealing of sample films above its glass transition temperature of the polymer could enhance surface segregation to a

certain extent in some blend systems.<sup>8,9</sup> However, annealing is not practically applicable in all circumstances. For example, degradation of the polymer may occur at elevated temperatures or the physical dimensions of the object being coated may be too large to be annealed. We have observed in our previous work<sup>10,16-19</sup> that the casting solvent in sample preparation significantly affects surface segregation. Polymer-solvent interaction properties and solvent evaporation rates have been found to be factors that influence this process, but complete PDMS covered surfaces have not been observed for low PDMS content polymer blends using a pure solvent in sample film preparation.<sup>5,10,19</sup> In the present study, binary solvent mixtures were investigated for casting solvent effects on surface segregation of PDMS polymer blends. Solvent systems were selected based on our previous studies,<sup>16</sup> in particular cyclohexanone/chloroform and toluene/chloroform mixtures were investigated. The surface composition of PDMS-co-PS/PS diblock copolymer/homopolymer blends has been studied at wide range of sampling depths using ToF SIMS, XPS and ATR FTIR.

## Experimental Section

**Materials and Sample Preparation.** Diblock copolymer poly(dimethylsiloxane)-co-polystyrene (PDMS-co-PS) was provided as a donation by Dr. Dale Meier of Michigan Molecular Institute, Midland, MI. Number average molecular weights of PDMS-co-PS are 70000 for PS block and 99000 for PDMS block, respectively. A standard reagent of trimethylsilyl terminated polystyrene (PS) with narrow molecular weight distribution was purchased from Scientific Polymer Products, Inc. Polystyrene ( $M_n=280,000$ ) was purchased from Aldrich (Milwaukee, WI). Reagent grade solvents were used in this study, in particular, chloroform was

purchased from EM Science (Gibbstown, NJ), toluene and cyclohexanone (HPLC grade) were purchased from Aldrich. All polymers and solvents were used as received. Binary solvents were mixed by volume percentage (Table 1). Polymer sample films were solution cast in aluminum weighing pans from 1% (w/v) solutions of each solvent composition. The cast films were allowed to air-dry at room temperature and stored in vacuum before analysis for removing solvent residue. The thickness of sample films was controlled to about 50 $\mu$ .

**XPS Analysis.** All survey and high resolution angle-dependent XPS spectra were recorded with a Perkin-Elmer Electronics 5300 XPS spectrometer with a hemispherical analyzer and a single channel detector. Mg K $\alpha_{1,2}$  X-rays were used as X-ray source, operated at 300w (15.0 kV and 20 mA). Base pressure in the main chamber was maintained no higher than  $5.0 \times 10^{-9}$  Torr. A survey spectrum from 0 to 1000 eV was recorded to each sample film prior to high resolution spectrum acquisition. All survey spectra were recorded at a rate of 1.0 eV/step with a take-off angle of 45 $^{\circ}$  and pass energy of 89.45 eV. High resolution spectra were acquired using angle-dependent mode for obtaining surface composition information at different depths. Five take-off angles were used, in particular 10, 15, 30, 45 and 90 degrees. The detection depths relevant to each take-off angle are listed in Table 2.<sup>5</sup> A pass energy of 35.75 eV and a scan energy resolution of 0.20 eV/step were used for all high resolution XPS spectra acquisitions with a 20 eV scanning range. No radiation damage was observed during twice the time of an XPS spectrum acquisition, as evidenced from no change in XPS spectra and no discoloration observed. At least three high-resolution acquisitions were performed for each sample.

**ToF SIMS Analysis.** Positive secondary ion mass spectrometry spectra were

acquired on a Physical Electronics 7200 time-of-flight secondary ion mass spectrometer (ToF SIMS) equipped with a cesium ion gun and a multichannel detector. The primary ion gun was operated at 8keV in all spectral acquisitions. The static mode was used in all acquisitions with primary ion current of 0.3 pA. The total ion dosage in each spectrum acquisition was no more than  $1 \times 10^{11}$  ion/cm<sup>2</sup>. A neutralizer was operated in all spectrum acquisition in pulse mode at low electron energy with a target current under 1  $\mu$ A for charge compensation. Data reduction was performed using Physical Electronics TOFPak software (version 2.0). Relative peak intensities were obtained by converting the spectra to ASCII file format and integrating peak area using the data analysis function built-in in Origin™ (Microcal Software, Inc. Northampton, MA).

**ATR FT-IR Analysis.** All ATR FT-IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer, using resolution of 4 cm<sup>-1</sup>, purged with nitrogen to ensure a stable and identical data collection environment. 500 scans were performed for each spectrum in all ATR FTIR acquisitions. A Harrick Scientific variable-angle multi-reflection ATR accessory (model X) and Germanium prisms (refractive index 4.0) were used. Taking effective thickness as the detection depth in ATR FTIR analysis,<sup>20,21</sup> a detection depth of 0.68  $\mu$ m was estimated for the incident angle of 45°.<sup>22</sup> As in XPS analysis, each sample was measured at least three times.

## **Data Analysis of Experimental Results**

**Recalibration of XPS Si 2p Sensitive Factor.** The accuracy of sensitivity factors used in determining the atomic percentage is crucial in XPS quantitative analysis. Incorrect sensitivity factors would result in inaccurate atomic percentages and cause larger errors in the calculation of

atomic ratios, and consequently reduce the reliability of XPS quantitation results. Recalibration of sensitivity factors including carbon 1s, oxygen 1s and silicon 2s on this particular instrument has been done in our previous work.<sup>23</sup> The sensitivity factor for silicon 2p was recalibrated based on our previously determined values for carbon 1s, oxygen 1s and silicon 2s. Pure PDMS (trimethylsilyl terminated, Polymer Scientific Laboratories) was used for the calibration of silicon 2p sensitivity factor. Thick films of PDMS (about 5 $\mu$ ) were solution cast on silver substrate using pure chloroform as solvent. Calibration films were cast under nitrogen protection and solvent evaporated directly in XPS spectrometer prechamber to eliminate possible contamination during solvent evaporation. High resolution XPS spectra were taken on carbon 1s, oxygen 1s, silicon 2s and silicon 2p. Atomic concentration results of XPS on carbon 1s, oxygen 1s and silicon 2s using our previously calibrated sensitivity factors<sup>23</sup> agree with the stoichiometry of PDMS within  $\pm 2\%$ . The sensitivity factor for silicon 2p was then calculated based on carbon 1s and oxygen 1s XPS data and the stoichiometry of PDMS. All sensitivity factors used in this study are shown in Table 3.

**XPS Results.** High-resolution spectra of carbon 1s, oxygen 1s and silicon 2p were recorded for quantitative XPS analysis. Atomic ratios of carbon and silicon were used in the quantitation. According to the structures of the repeat units of PS (contains eight carbon atoms in each repeat unit) and PDMS (contains two carbon atoms and one silicon atom) segments, the surface DMS molar fraction is expressed in equation 1 in terms of the carbon/silicon atomic ratio as

$$X_{\text{DMS}} = \frac{8}{6 + \text{C/Si}} \quad (1)$$



in which C and Si are the atomic percentages of carbon and silicon from XPS measurements, respectively.<sup>5,25</sup> The integration of high-resolution peaks was performed using a Perkin Elmer Model 7500 professional computer running PHI version 2.0 ESCA software.

**ATR FTIR Results.** ATR FTIR analysis provides a complementary result to XPS at an extended detection depth. The accuracy of quantitation of ATR FTIR analysis depends heavily on the calibration method. Pre-defined stratification structures are widely used as model system for calibration for quantitation.<sup>34</sup> However, because of the unknown nature of composition depth gradient in our samples, a pre-defined stratification structure cannot serve as a calibration standard in the present study. A new ATR FTIR quantitation procedure suitable for polymer blend systems with unknown surface chemical composition gradient has been developed in our laboratory.<sup>22</sup> A brief outline of this procedure is given here.

The calibration is based on transmission calibration on standard films with known chemical composition and thickness. The recorded transmission spectra were corrected for pathlength dependence according to the penetration depth<sup>20</sup> in ATR measurements (Eq 2).

$$d_p = \frac{\lambda_d}{2\pi[\sin^2 \theta - (\frac{n_1}{n_d})^2]^{1/2}} \quad (2)$$

A calibration curve was created from the transmission spectra of standard sample files (Solid line in Figure 1). Also shown in Figure 1 is a calibration curve (Dashed line in Figure 1) calculated based on Beer's law using the data from the two pure samples only, which indicates that the

blending of the two polymers does not cause any physical or chemical interaction that influences their IR absorption properties. A calibration equation was obtained using polynomial regression (also shown in Figure 1). This calibration curve was used throughout ATR FTIR quantitative analysis in this study.

Before peak integration on sample ATR spectra is performed, all ATR spectra were corrected for radiation penetration depth dependence of wavelength and for physical contact quality.<sup>20</sup> The peak area of selected peaks were integrated using the GRAMS/386 software (Galactic Industries Corporation, Salem, NH). Surface chemical composition was then obtained using the calibration equation.

**ToF SIMS Results.** Positive ToF SIMS spectra were recorded for determining chemical composition on a much shallower surface layer, in particular, the top-most few atomic layers. The high sensitivity of ToF SIMS makes this technique an ideal method for trace analysis. Figure 2 shows the low mass portion ToF SIMS spectra of a pure PDMS film on aluminum substrate (Figure 2a) and a typical blend sample thick film (Figure 2b, about 50 $\mu$  thick free standing film which contains 2% PDMS, cast from binary solvent of 5% cyclohexanone in chloroform by volume). The peak at  $m/z=73.048$  is the most intense peak for both pure PDMS and the polymer blend sample. In the mass range below  $m/z=60$  in the spectra of polymer blend samples, in particular, peaks at 28 ( $\text{Si}^+$  atomic peak), 43 ( $\text{CH}_3\text{Si}^+$ ), and 59 ( $\text{CH}_3\text{OSi}^+$ ), have stronger peak intensities relative to the peak at  $m/z=73.048$  than in the spectra of pure PDMS thin film. This is presumably due to the highly entangled molecular structure for thick films of polymer blends compared to the thin film molecular structure of pure PDMS on substrates. For

the same reason, the relative intensities of higher mass peaks ( $m/z$  higher than 73) are lower for the blend sample. It should be noted that, due to stabilization effects,<sup>26</sup> the relative peak intensities for cyclic structure fragments (peaks of  $m/z$  207 and higher) become stronger than the fragments from linear structure, and this effect is more pronounced for spectra from blend samples than that from the pure PDMS. We believe this is due to the highly entangled molecular structure in thick films which requires higher energy in forming secondary ion fragments that makes fragments less stable than that from thin films.

What we wish to demonstrate is whether a complete PDMS segment layer has formed on the blend surface at the ToF SIMS detection depth. Secondly we wish to examine solvent effects on surface segregation at that sampling depth. It is well known that the dominant peak in the spectra of PS is at  $m/z=91.055$ , due to the tropylium cation  $C_7H_7^+$  rearranged from a styrene sidechain.<sup>29,31</sup> Although it is not exclusively characteristic for PS, this peak can be used in this system to track the existence of PS on sample surfaces since PDMS does not have an aromatic ring structure. We have observed, although there is only very low intensity relative to the peak at  $m/z=73.048$ , that the tropylium cation fragment peak does exist in all ToF SIMS spectra we collected. Thus small amounts of PS are still detectable by ToF SIMS.

More importantly, remarkable differences on surface composition have been observed in the spectra from films cast from different solvent mixtures. By taking the relative peak intensity of characteristic peaks of PDMS and PS in the ToF SIMS spectra we were also able to describe the trend in solvent effects on surface segregation on the top few atomic layers.<sup>33</sup>

## Results and Discussion

Table 4 lists all results of surface DMS concentration of the PDMS-co-PS/PS diblock copolymer/homopolymer blend films cast from different solvents by both XPS and ATR FTIR quantitative analysis. Surface PDMS concentration data are provided in molar fraction of DMS repeat units, followed with standard deviation (in parenthesis) to show the reproducibility of the quantitative analysis results. Discussion on the results below will highlight some of the important features.

Figure 3 shows the surface DMS concentration versus bulk DMS concentration from XPS data of  $10^\circ$ ,  $30^\circ$  and  $90^\circ$  of take-off angles of pure chloroform cast films. At the shallowest sampling depth ( $10^\circ$  take-off angle which corresponding to  $18\text{\AA}$  of sampling depth), the surface DMS concentration increases quickly from 92% for 1% bulk PDMS sample to 95% for 2% bulk PDMS sample, then reaches 98% for 3% bulk PDMS sample where the surface PDMS concentration levels off. At deeper layers, the changes in surface PDMS concentration are even more pronounced. For instance, at  $103\text{\AA}$  the surface PDMS concentration increases from 73% for 1% bulk PDMS sample to 85% for 2% bulk PDMS sample indicating a thicker region of surface segregation. However, the fact that the surface PDMS concentration levels off at 3% bulk PDMS concentration indicates that further increases in bulk PDMS concentration will not significantly increase the surface PDMS concentration, although they may result in a thicker PDMS rich region. We have previously reported<sup>16</sup> the extent of surface segregation of PDMS in polymer blends using different pure solvents. Although solvents used in film preparation influence the process of surface segregation significantly, we have never observed 100% surface PDMS concentration for low bulk PDMS concentration (<3%) in PS blends.

**The Influence of Polymer-solvent Interaction on Surface Segregation.** In considering the mixing thermodynamics of polymers with solvents, PDMS has an opposite interaction characteristic with many common solvents compared with PS. This behavior can be explained using polymer-solvent interaction parameters<sup>27</sup> ( $\chi$ ). For example, when the  $\chi$  parameter is plotted versus polymer volume fraction in solution, PDMS shows an increasing trend in toluene as the concentration of the solution increases, while PS shows a declining trend. This suggests that during solvent evaporation, the mobility of PDMS segments will decrease faster than PS due to solvation of polymer segments in solution. However, the  $\chi$  parameter of PDMS in chloroform is essentially unchanged while the polymer volume fraction increases from 0 to 1 (Figure 4). It can be expected that, if a poor solvent for PDMS is mixed with chloroform, the decrease in mobility of PDMS segments makes the cohesive migration of PS segments more efficient, therefore encouraging preferential precipitation of PDMS segments and resulting in higher surface segregation, while PS segments still retain high mobility. This is exemplified by samples cast from chloroform/toluene mixtures. Figure 5 shows surface PDMS concentration dependence of toluene concentration in binary solvent mixtures. At the XPS detected top-most layer, the surface PDMS concentration increased from 92% (cast from pure chloroform) to 95% (cast from both 20% and 30% toluene mixtures) for samples with 1% bulk PDMS concentration. For 2% bulk PDMS concentration samples, the surface PDMS concentration increased from 95% (cast from pure chloroform) to virtually 100% (cast from 30% toluene mixture). The results show that surface DMS concentration varies substantially depending on solvent composition.

**Solvent Polarity Effect on Surface Segregation.** It has been observed in previous

studies that solvents with higher boiling points could increase surface segregation, presumably due to the prolonged solvent evaporation time. For example, when pyridine was used as casting solvent in the preparation of BPAC-PDMS copolymer sample films, the surface PDMS concentration of as-cast films is higher (90%) than the same copolymer cast from ethylene chloride<sup>24</sup> (88%). However, annealing did not make a detectable increase in surface DMS concentration for films cast from pyridine. In contrast, annealing methylene chloride cast films increased surface DMS from 88% to 92%. This phenomenon was understood as the lower solvent evaporation rate of pyridine provides longer time for polymer segments to move around toward thermodynamic equilibrium before the polymer matrix solidifies. In the present study, up to 10% cyclohexanone was mixed with chloroform to form binary solvents. Figure 6 shows the solvent dependence of surface DMS concentration for 1% bulk PDMS content samples (Figure 6a) and 2% bulk PDMS content samples (Figure 6b), respectively. The graphs show that surface PDMS concentration first increases as the concentration of cyclohexanone increase, and then peaks and declines. This phenomenon cannot be interpreted simply as the extension of solvent evaporation time.

By considering the polarity of the solvent, the surface segregation behavior of PDMS in this solvent can be understood. For example, the polarity term in Hansen parameters<sup>27</sup> for chloroform is 3.1 while that for cyclohexanone is 6.3 (Table 5). There is a strong local polarity for PDMS along the silicon-oxygen bond due to the difference in electronegativity of the two elements (gas phase dipole moment of OSi 3.1D<sup>32</sup>). Compared with PDMS, the local polarity in polystyrene is much weaker (local polarity in PS is along the axis of the aromatic ring structure, which has a gas phase dipole moment 0.38D<sup>32</sup>). When cyclohexanone is mixed with chloroform

in small portions, the solvation of cyclohexanone molecules would selectively occur around PDMS segments. The better solvated PDMS segments helps the surface segregation of PDMS and cohesive migration of PS toward the bulk more efficiently. It is interesting to note that for lower bulk PDMS content samples (1% bulk PDMS), the surface PDMS concentration peaks at lower cyclohexanone concentration than samples with higher bulk PDMS concentration. This suggests that selective solvation of PDMS segments by cyclohexanone is the key issue. It could be predicted that when an excess amount of cyclohexanone exists in the solvent, the solvation of PS segments by cyclohexanone molecules is also increased, which makes surface segregation of PDMS less efficient.

Different from the toluene/chloroform binary solvents, which enhance surface segregation through selective precipitation, cyclohexanone promotes surface segregation by selective solvation of PDMS segments, and thus the surface segregation would be expected to extend to deeper layers. Figure 7 and 8 show surface PDMS concentration of 1% and 2% bulk PDMS content sample at greater depth by ATR FTIR measurements. The fact that surface PDMS concentration of cyclohexanone mixture cast samples is about 8% higher than samples cast from toluene mixtures at this detection depth indicates the active segregation region is much broader than that in the former case. Furthermore, there is no significant difference in surface PDMS concentration between 1% and 2% bulk PDMS content in cyclohexanone/chloroform cast samples, while the difference in toluene-mixture cast sample is very pronounced. This also serves as evidence that the active surface segregation region in cyclohexanone/chloroform cast films is thicker than films cast from the toluene mixtures.

**Depth Profile.** The difference in mechanisms of promoting surface segregation by

solvents can also be seen by considering the in-depth profile of PDMS concentration produced by combining results from different methods. For toluene-containing solvent mixtures, the unfavorable polymer-solvent interaction property between toluene and PDMS segments causes preferential precipitation. This limits surface segregation to a narrower range in depth from the surface. In contrast, the existence of cyclohexanone in solvent increases the degree of solvation around PDMS segments, therefore polymer segments could keep significant mobility even when very little solvent left in polymer. This is exemplified by Figure 9, a plot of detected PDMS concentration versus depth over a wide sampling range by XPS and ATR FTIR. Throughout the broad depth range, PDMS concentration detected on the surface is higher for films cast from cyclohexanone mixtures than that cast from toluene binary solvent without an exception. At deeper layers detected by ATR FTIR, the difference in PDMS concentration appears to be even greater than at the shallower layers measured by XPS.

**Surface Composition by ToF SIMS Analysis.** Although 100% PDMS has been observed on sample surfaces using XPS, we can not rule out the possibility that trace amounts of PS residue remain on the surface due to the relatively low sensitivity of XPS as compared with ToF SIMS. Taking the advantage of ppm sensitivity of ToF SIMS, we not only detected very small amount of PS residues on the top few atomic layers of the surface, but also clearly observed the solvent effects on surface segregation by measuring the relative peak intensities of trimethylsilyl cation ( $m/z=73.048$ ) and tropylium cation ( $m/z=91.055$ ). Relative peak intensities from samples all containing 2% PDMS in bulk and cast from different solvents are listed in Table 6. The surface PS concentration differences due to casting solvents can be quantitatively evaluated as the ratio of relative peak intensities as shown in Table 6. These results are consistent



with that from XPS and ATR FTIR quantitation. Figure 10 shows ToF SIMS images of surface PDMS and PS represented by fragments of trimethylsilyl cations and tropylium cations. Data illustrated by the images show that the distribution of PS residues is also different. Larger microdomains may exist on surfaces of pure chloroform cast films, while binary solvent cast films have much smaller microdomains of PS.

**End-group Preferential Orientation.** Previous studies of PDMS by both mass spectrometry<sup>28</sup> and SIMS<sup>29</sup> suggested that the trimethylsilyl fragment ( $\text{Si}(\text{CH}_3)_3^+$ ) results from rearrangements of PDMS backbone chain fragments. However, a more recent study on PDMS<sup>30</sup> and then poly(methylphenylsiloxane)<sup>31</sup> (PMPS) suggests the  $\text{Si}(\text{CH}_3)_3^+$  fragment may come solely from the trimethylsilyl end-group. In PMPS samples that are not terminated by trimethylsilyl, the  $\text{Si}(\text{CH}_3)_3^+$  fragment was not detected.<sup>31</sup> Clarson and co-workers also attributed the high intensity of  $\text{Si}(\text{CH}_3)_3^+$  to end-group enrichment due to the low surface energy and large free volume of the trimethylsilyl group. Therefore, a comparison of fragment peak intensities of higher mass species among samples prepared with different methods would help to distinguish if casting solvent effects end-group preferential orientation only or PDMS segments in surface segregation. The  $m/z=73$ , 147, and 221 fragment series in PDMS has an exponential intensity-decay pattern. The  $m/z=147$  peak is due to  $\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3^+$ , one PDMS repeat unit longer than the trimethylsilyl end-group, and the peak at  $m/z=221$  is one more repeat unit longer than the  $m/z=147$  peak. Figure 11 shows the comparison of the relative intensities in this series from samples cast by different solvents. Figure 11a is the spectrum from a pure PDMS monolayer film cast on an aluminum substrate. In a monolayer, the polymer chain can be considered as laying flat on the substrate and the end-group preferential orientation effect at the polymer surface is

eliminated. Therefore it can be considered that the fragmentation from a monolayer film is not to be affected by end-group preferential orientation effects. Figure 11b, c. and d are spectra of blend sample thick films of 2% bulk PDMS content, cast from pure chloroform, 20% toluene in chloroform, and 7% cyclohexanone in chloroform, respectively. Figure 11a has the highest relative intensity of peak  $m/z=147$  to 73, suggesting higher ion yield of longer segment fragments from flat laying polymer molecules on substrate. Based on this, we could assume that higher relative intensity of these two peaks means more PDMS segments exist on the sample surface. Figure 11 suggests that the cyclohexanone binary solvent cast sample have the strongest relative intensity of these two peaks. It is not a surprise that the PDMS thin film on substrate gives the highest relative intensity because of the chain entanglement in thick polymer films. This trend holds for the higher  $m/z$  peaks in this sequence. This means that PDMS segments, not only the trimethylsilyl end-group, exist at the top-most layer, and the surface structure is indeed solvent dependent.

## Conclusion

The surface composition of PDMS-co-PS/PS diblock-copolymer/homopolymer blends has been studied in detail over a wide range of detection depths using XPS, ATR FTIR and ToF SIMS. Solvent effects on the surface segregation process are revealed. A complete PDMS segment layer surface coverage is achieved using binary solvent mixture of chloroform and cyclohexanone with 2% bulk PDMS content. A further increase of bulk PDMS concentration does not make detectable increase in surface PDMS concentration. For samples containing less than 2% bulk PDMS content, the surface PDMS concentration difference is detectable at

different depth of measurements. ToF SIMS measurements reveal that a complete surface PDMS layer has formed via surface segregation in cyclohexanone binary solvent cast films. Small amounts of PS segment residue can be detected on sample surfaces by ToF SIMS to both toluene-containing binary solvent and pure chloroform cast films.

Evidence shows through ToF SIMS spectra that casting solvent during the sample preparation has also changed the surface morphology. The solvent effects on surface morphology in the top-most layer need to be further investigated.

## References

- (1) Jarvis, N. L.; Fox, R. B. and Zisman, W. A. *Adv. Chem. Ser.* **1964**, *43*, 317.
- (2) Owen, M. J. *Commun. Inorg. Chem.* **1988**, *7*, 195.
- (3) Yilgor, I. and McGrath, J. E. *Adv. Polym. Sci.* **1988**, *86*, 1.
- (4) Owen, M. J. In *Siloxane Polymers*, Clarson, S. J. and Semlyen, J. A. Eds. Prentice Hall, Englewood Cliffs, NJ. 1993.
- (5) Chen, X.; Kumler, P. L. and Gardella, J. A. Jr. *Macromolecules* **1992**, *25*, 6621.
- (6) Chen, X.; Kumler, P. L. and Gardella, J. A. Jr. *Macromolecules* **1992**, *25*, 6631.
- (7) Gardella, J. A. Jr.; Ho, T.; Wynne, K. J. and Zhuang, H.-Z. *J. Colloid and Interface Science* **1995**, *176*, 277.
- (8) Chen, X.; Lee, H. F. and Gardella, J. A. Jr. *Macromolecules* **1993**, *26*, 4601.
- (9) Chen, X.; Gardella, J. A. Jr. and Kumler, P. L. *Macromolecules* **1993**, *26*, 3778.
- (10) Chen, X. and Gardella, J. A. Jr. *Macromolecules* **1994**, *27*, 3363.
- (11) Chen, X.; Gardella, J. A. Jr.; Ho, T. and Wynne, K. J. *Macromolecules* **1995**, *28*, 1635.
- (12) Dwight, D. W.; McGrath, J. E.; Riffle, J. S.; Smith, S. D. and York, G. A. *J. Electron Spectrosc.* **1990**, *52*, 457.
- (13) LeGrand, D. G. and Gaines, G. L. *Polym. Prepr. Am. Chem. Soc.* **1970**, *11*, 442.
- (14) Gaines, G. L. and Bender, G. W. *Macromolecules* **1972**, *5*, 82.
- (15) Gaines, G. L. *Macromolecules* **1979**, *12*, 1011.
- (16) Chen, J.-X. and Gardella, J. A. Jr. *PMSE Prepr. Am. Chem. Soc.* **1994**, *71*, 447.
- (17) Chen, J.-X. and Gardella, J. A. Jr. *PMSE Prepr. Am. Chem. Soc.* **1996**, *75*, 404.
- (18) Schmidt, J. J.; Gardella, J. A. Jr. and Salvati, L. Jr. *Macromolecules* **1989**, *22*, 4489.
- (19) Chen, J.-X.; Zhuang, H.-Z. and Gardella, J. A. Jr. *Critical Reviews in Surface Chemistry*, Submitted Feb. 1998.

- (20) Harrick, N. J. *Internal Reflection Spectroscopy*. John Wiley & Sons. New York, 1979.
- (21) Mirabella, F. and Harrick, N. J. *Internal Reflection Spectroscopy: Review and Supplement*. Harrick Scientific Co., Ossining NY, 1985.
- (22) Chen, J.-X. and Gardella, J. A. Jr. *Applied Spectroscopy*, **1998**, in press.
- (23) Vargo, T. G. and Gardella, J. A. Jr. *J. Vac. Sci. Technol.* **1989**, *A7*, 1733.
- (24) Zhuang, H.-Z. and Gardella, J. A. Jr. *Macromolecules* **1997**, *30*, 3632.
- (25) Schmitt, R. L.; Gardella, J. A. Jr.; Chin, R. L.; Magill, J. H.; and Salvati, L. Jr. *Macromolecules* **1985**, *18*, 2675.
- (26) Xia, D.; Proctor, A. and Hercules, D. M. *Macromolecules* **1997**, *30*, 63.
- (27) *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*. Barton A. F. M., CRC Press, Boston, 1990.
- (28) Ballistreri, A.; Garozzo, D. and Montaudo, G. *Macromolecules* **1984**, *17*, 1312.
- (29) Bletsos, I. V.; Hercules, D. M.; vanLeyen, D. and Benninghoven, A. *Macromolecules* **1987**, *20*, 407.
- (30) Selby, C. E.; Stuart, J. O.; Clarson, S. J.; Smith, S. D.; Sabata, A.; van Ooij, W. J. and Cave, N. G. *Journal of Inorganic and Organometallic Polymers* **1994**, *4*, 85.
- (31) Clarson, S. J.; Stuart, J. O.; Selby, C. E.; Sabata, A.; Smith, S. D. and Ashraf, A. *Macromolecules* **1995**, *28*, 674.
- (32) *CRC Handbook of Chemistry and Physics*, Lide, D. R. Editor-in-Chief. CRC press, 73rd Ed., 1992.
- (33) Weng, L. T. and Bertrand, P. *Surface and Interface Analysis* **1995**, *23*, 879.
- (34) Ekgasit S. and Ishida H. *Applied Spectroscopy* **1996**, *50*, 1187.

## Caption of figures

- Figure 1. ATR FTIR quantification working curve from transmission calibration.
- Figure 2. The low mass portion of positive ToF SIMS spectra of pure PDMS thin film (a) and polymer blend thick film (b).
- Figure 3. Surface DMS versus bulk DPS concentration by XPS at different detection depth. Sample films cast from pure chloroform.
- Figure 4. Polymer-solvent interaction parameter  $\chi$  versus polymer molar fraction. Data taken from ref. 27.
- Figure 5. Surface DMS versus toluene concentration by XPS. a. 1% bulk DMS content; b, 2% bulk DMS content.
- Figure 6. Surface DMS versus cyclohexanone concentration by XPS. a. 1% bulk DMS content; b. 2% bulk DMS content.
- Figure 7. Surface DMS versus cyclohexanone concentration in solvent by ATR FTIR at detection depth of  $0.7\mu$ .
- Figure 8. Surface DMS versus toluene concentration in solvent by ATR FTIR at detection depth of  $0.7\mu$ .
- Figure 9. Surface DMS depth gradient by XPS and ATR FTIR. a. cast from 7% cyclohexanone in chloroform. b. cast from 20% toluene in chloroform.
- Figure 10. ToF SIMS image of samples cast from different solvents.
- Figure 11. Log plot of ToF SIMS spectra from of  $m/z=60$  to 160. a. pure PDMS thin film on aluminum; b, polymer blend cast from pure chloroform; c. polymer blend cast from 20% toluene in chloroform; d, polymer blend cast from 7% cyclohexanone in chloroform. Sample b through d all contain 2% PDMS in bulk.

**Table 1. Solvent Composition**

Solvent	chloroform (% by volume)	Second component
#0	100	
Toluene		
#1	95	5
#2	90	10
#3	80	20
#4	70	30
Cyclohexanone		
#5	98	2
#6	95	5
#7	93	7
#8	90	10

Table 2. ESCA detection depth<sup>5</sup>

Take-off angle (degree)	10	15	30	45	90
Sampling depth (Angstrom)	18	27	52	73	103



Table 3. XPS Sensitivity Factors

Carbon 1s	Oxygen 1s	Silicon 2p
0.24	0.65	0.24

**Table 4. Surface PDMS concentration (in DMS molar %)**

Bulk DMS mol %	Solvent <sup>a</sup> Toluene V%	at depth <sup>b</sup>					
		18A (± SD)	27A (± SD)	52A (± SD)	73A (± SD)	103A (± SD)	700A (± SD)
1.0	0.0	92.4 ( 1.0 )	89.5 ( 1.1 )	83.7 ( 1.0 )	78.9 ( 1.0 )	73.4 ( 1.0 )	9.0 ( 5.0 )
1.0	5.0	92.6 ( 1.3 )	92.4 ( 1.0 )	87.3 ( 1.0 )	82.2 ( 1.0 )	74.8 ( 1.0 )	14.0 ( 5.0 )
1.0	10.0	94.5 ( 1.0 )	91.6 ( 1.0 )	87.7 ( 1.0 )	80.9 ( 1.0 )	78.4 ( 1.0 )	14.9 ( 5.0 )
1.0	20.0	94.9 ( 1.0 )	91.6 ( 1.0 )	88.4 ( 1.0 )	86.5 ( 1.0 )	81.8 ( 1.0 )	16.6 ( 5.0 )
1.0	30.0	95.4 ( 1.0 )	92.6 ( 1.0 )	87.9 ( 1.0 )	82.2 ( 1.0 )	75.6 ( 1.0 )	16.9 ( 5.0 )
2.0	0.0	95.1 ( 1.3 )	93.7 ( 1.0 )	92.2 ( 1.0 )	89.5 ( 1.0 )	84.9 ( 1.0 )	15.1 ( 5.0 )
2.0	5.0	95.8 ( 1.1 )	95.1 ( 1.0 )	93.6 ( 1.4 )	91.4 ( 1.0 )	88.2 ( 1.0 )	20.3 ( 5.0 )
2.0	10.0	96.3 ( 1.0 )	95.8 ( 1.0 )	95.2 ( 1.0 )	92.9 ( 1.0 )	90.0 ( 1.0 )	22.6 ( 5.0 )
2.0	20.0	97.9 ( 1.0 )	97.0 ( 1.0 )	96.0 ( 1.2 )	92.5 ( 1.4 )	89.6 ( 1.0 )	26.2 ( 5.0 )
2.0	30.0	99.6 ( 1.0 )	98.0 ( 1.1 )	95.0 ( 1.6 )	90.6 ( 1.0 )	86.4 ( 1.0 )	23.8 ( 5.0 )
3.0	0.0	97.9 ( 1.0 )	97.7 ( 1.0 )	97.0 ( 1.0 )	94.5 ( 1.0 )	91.8 ( 1.0 )	20.3 ( 5.0 )
3.0	5.0	98.0 ( 1.3 )	96.7 ( 1.0 )	95.7 ( 1.0 )	93.9 ( 1.0 )	89.5 ( 1.0 )	27.4 ( 5.0 )
3.0	10.0	98.0 ( 1.0 )	97.2 ( 1.0 )	96.2 ( 1.6 )	93.9 ( 1.0 )	90.0 ( 1.0 )	29.5 ( 5.0 )
3.0	20.0	98.6 ( 1.0 )	98.2 ( 1.0 )	95.7 ( 1.0 )	92.2 ( 1.0 )	87.8 ( 1.0 )	30.8 ( 5.0 )
3.0	30.0	99.4 ( 1.0 )	98.0 ( 1.0 )	94.2 ( 1.5 )	88.7 ( 1.0 )	81.2 ( 1.0 )	31.2 ( 5.0 )
4.0	0.0	98.5 ( 1.2 )	98.2 ( 1.0 )	97.3 ( 1.0 )	95.1 ( 1.0 )	91.9 ( 1.0 )	33.4 ( 5.0 )
4.0	5.0	98.6 ( 1.0 )	98.2 ( 1.0 )	96.8 ( 1.0 )	94.3 ( 1.0 )	91.1 ( 1.0 )	33.8 ( 5.0 )
4.0	10.0	98.1 ( 1.0 )	97.1 ( 1.0 )	95.3 ( 1.1 )	94.0 ( 1.0 )	89.5 ( 1.4 )	35.2 ( 5.0 )
4.0	20.0	97.5 ( 1.4 )	94.8 ( 1.0 )	92.5 ( 1.0 )	89.2 ( 1.2 )	84.1 ( 1.0 )	40.0 ( 5.0 )
4.0	30.0	97.6 ( 1.2 )	96.7 ( 1.0 )	95.2 ( 1.0 )	92.5 ( 1.0 )	88.6 ( 1.0 )	43.5 ( 5.0 )
Cyclohexanone							
	V%						
1.0	0.0	92.4 ( 1.0 )	89.5 ( 1.1 )	83.7 ( 1.0 )	78.9 ( 1.0 )	73.4 ( 1.0 )	9.0 ( 5.0 )
1.0	2.0	96.4 ( 1.0 )	97.2 ( 1.0 )	93.8 ( 1.0 )	93.5 ( 1.0 )	83.5 ( 1.0 )	23.2 ( 5.0 )
1.0	5.0	98.0 ( 1.0 )	97.2 ( 1.0 )	95.3 ( 1.0 )	91.5 ( 1.0 )	87.9 ( 1.0 )	28.7 ( 5.0 )
1.0	7.0	96.8 ( 1.0 )	96.2 ( 1.0 )	94.9 ( 1.0 )	89.0 ( 1.0 )	86.0 ( 1.0 )	32.1 ( 5.0 )
1.0	10.0	96.6 ( 1.1 )	96.2 ( 1.0 )	93.0 ( 1.0 )	92.4 ( 1.0 )	82.9 ( 1.0 )	29.2 ( 5.0 )
2.0	0.0	95.1 ( 1.3 )	93.7 ( 1.0 )	92.2 ( 1.0 )	89.5 ( 1.0 )	84.9 ( 1.0 )	15.1 ( 5.0 )
2.0	2.0	99.4 ( 1.0 )	98.5 ( 1.0 )	95.8 ( 1.0 )	92.4 ( 1.0 )	88.0 ( 1.4 )	24.0 ( 5.0 )
2.0	5.0	100.3 ( 1.0 )	100.0 ( 1.0 )	98.4 ( 1.0 )	97.0 ( 1.0 )	94.5 ( 1.0 )	30.1 ( 5.0 )
2.0	7.0	100.2 ( 1.0 )	100.0 ( 1.0 )	99.0 ( 1.0 )	97.7 ( 1.0 )	94.6 ( 1.1 )	33.7 ( 5.0 )
2.0	10.0	98.8 ( 1.0 )	96.5 ( 1.0 )	92.6 ( 1.0 )	89.0 ( 1.0 )	85.3 ( 1.0 )	31.7 ( 5.0 )
3.0	0.0	97.9 ( 1.0 )	97.7 ( 1.0 )	97.0 ( 1.0 )	94.5 ( 1.0 )	91.8 ( 1.0 )	20.3 ( 5.0 )
3.0	2.0	99.1 ( 1.3 )	99.4 ( 1.3 )	98.2 ( 1.0 )	95.4 ( 1.0 )	91.8 ( 1.0 )	28.2 ( 5.0 )
3.0	5.0	100.1 ( 1.0 )	99.4 ( 1.0 )	98.8 ( 1.0 )	97.1 ( 1.0 )	94.9 ( 1.0 )	38.4 ( 5.0 )
3.0	7.0	99.7 ( 1.0 )	98.6 ( 1.5 )	97.6 ( 1.0 )	96.2 ( 1.0 )	93.1 ( 1.0 )	39.8 ( 5.0 )
3.0	10.0	98.6 ( 1.0 )	98.4 ( 1.0 )	96.9 ( 1.0 )	95.9 ( 1.0 )	91.8 ( 1.0 )	38.5 ( 5.0 )
4.0	0.0	98.5 ( 1.0 )	98.2 ( 1.0 )	97.3 ( 1.0 )	95.1 ( 1.0 )	91.9 ( 1.0 )	33.4 ( 5.0 )
4.0	2.0	98.8 ( 1.0 )	98.8 ( 1.0 )	98.0 ( 1.0 )	96.6 ( 1.0 )	94.1 ( 1.3 )	41.3 ( 5.0 )
4.0	5.0	99.4 ( 1.4 )	98.3 ( 1.2 )	98.2 ( 1.0 )	97.6 ( 1.1 )	95.8 ( 1.0 )	43.9 ( 5.0 )
4.0	7.0	97.8 ( 1.3 )	98.1 ( 1.2 )	98.2 ( 1.0 )	97.7 ( 1.0 )	94.5 ( 1.0 )	46.6 ( 5.0 )
4.0	10.0	97.2 ( 1.2 )	97.0 ( 1.4 )	95.3 ( 1.0 )	92.9 ( 1.0 )	88.9 ( 1.0 )	46.6 ( 5.0 )

a Binary solvent mixed with chloroform.

b XPS results except the last column, which is ATR FTIR results

**Table 5. Solubility Parameters of Solvents<sup>a</sup>**

Solvent	Hansen parameters	$\delta_d$	$\delta_p$	$\delta_h$	Hildebrand parameters
Chloroform	19	17.8	3.1	5.7	19
Toluene	18.2	18	1.4	2	18.2
Cyclohexanone	19.6	17.8	6.3	5.1	20.3

a. data adopted from ref. 27

**Table 6. Relative Surface PS  
Concentration of 2% Bulk PDMS Samples**

casting solvent	A73/A91 (SD)	relative surface PS concentration <sup>a</sup>
pure chloroform	47 (3)	0.049
20% toluene in chloroform	137 (8)	0.016
7% cyclohexanone in chloroform	562 (34)	0.004

<sup>a</sup> Taking the XPS result at 10° take-off angle of pure chloroform cast samples, the relative surface PS concentration are calculated based on ToF SIMS spectra peak ratios.

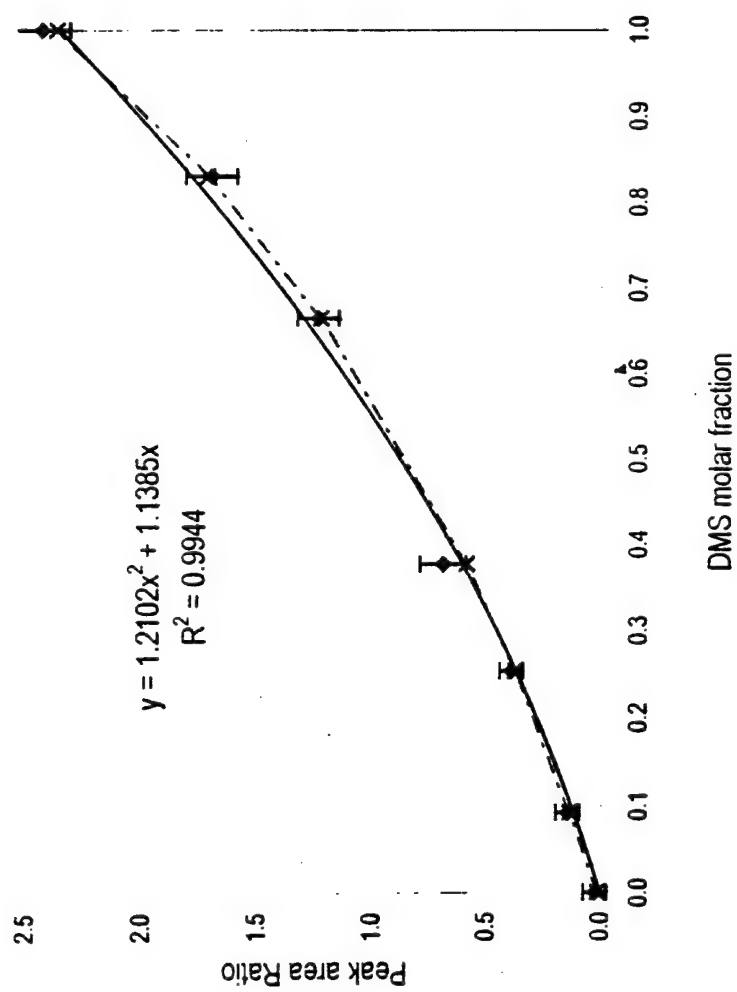
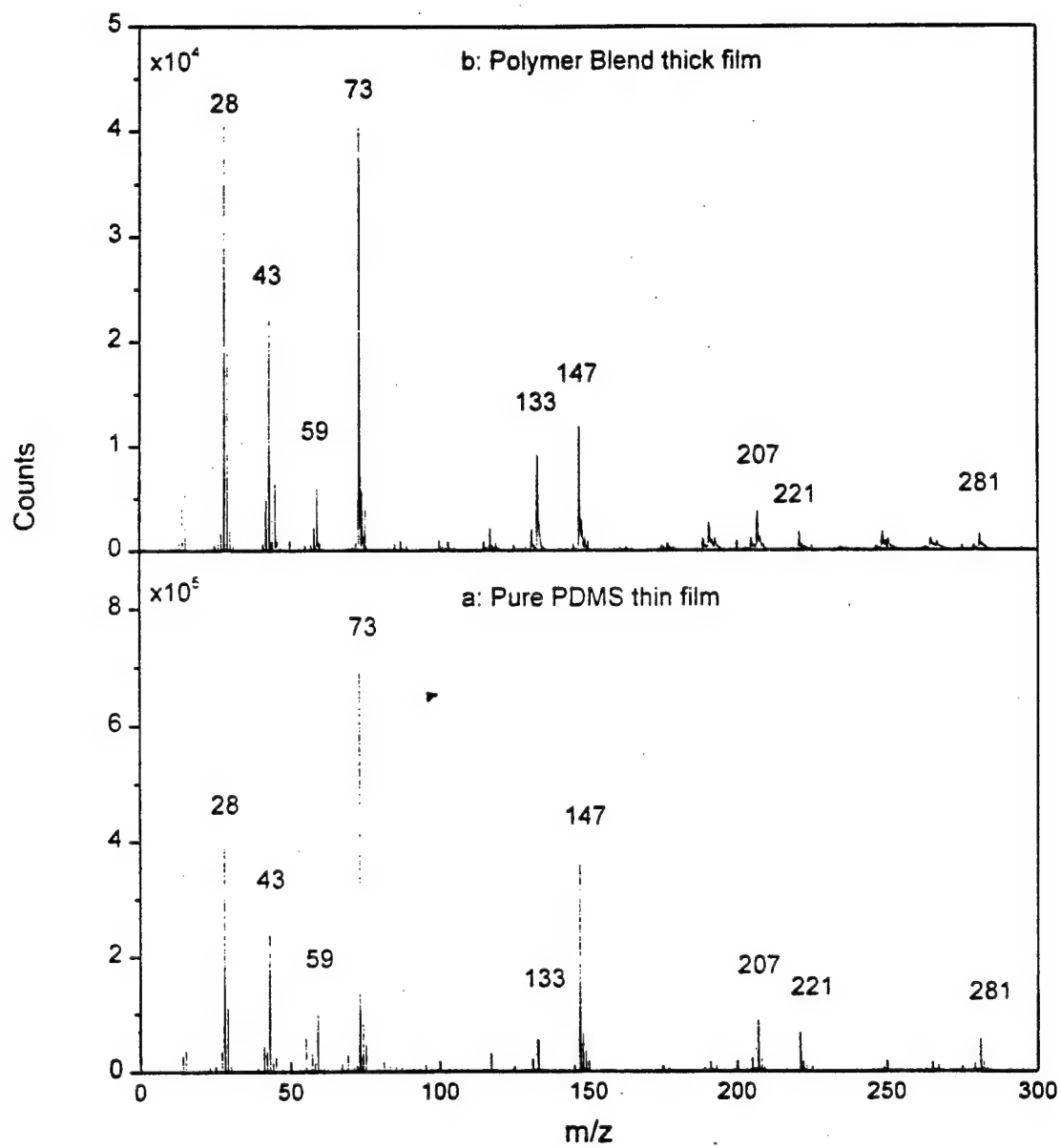


Figure 1 ATR FTIR quantification working curve from transmission calibration.



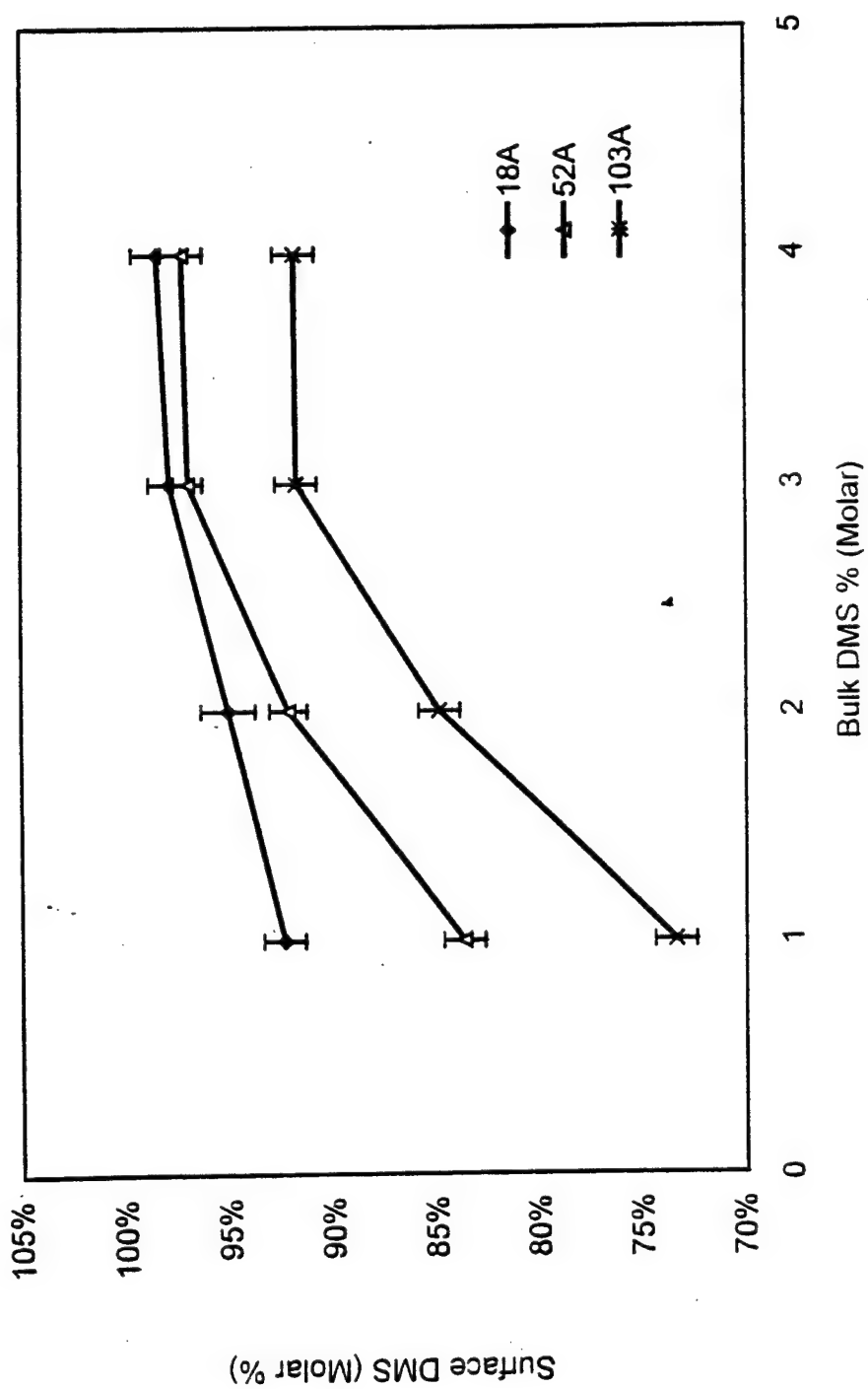
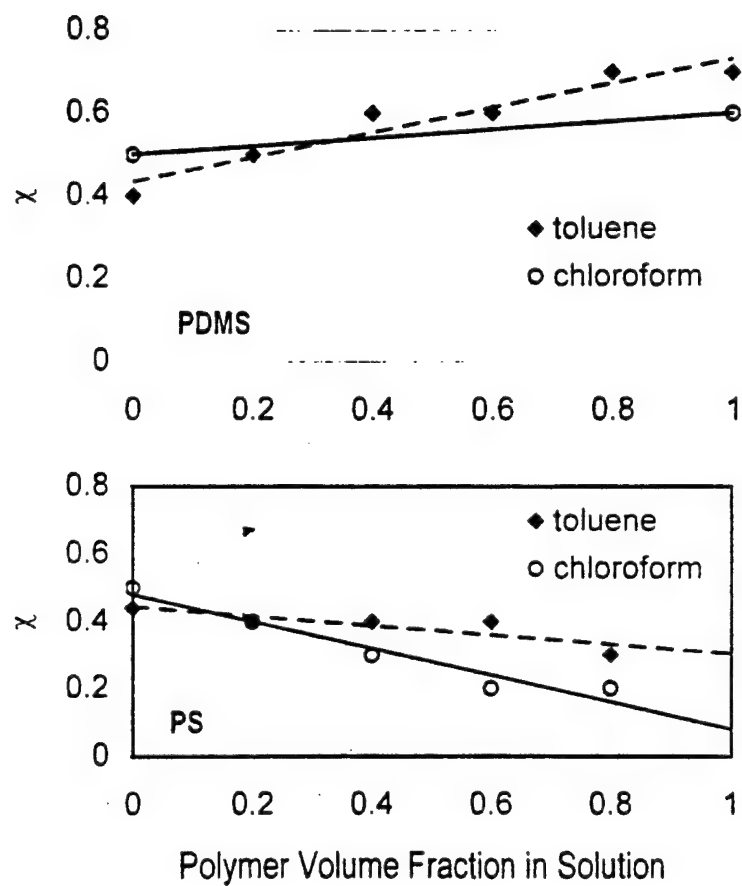


Figure 3 Surface DMS versus bulk DMS concentration by XPS Sample cast from pure chloroform.

Figure 4.  $\chi$  versus polymer molar fraction, ref



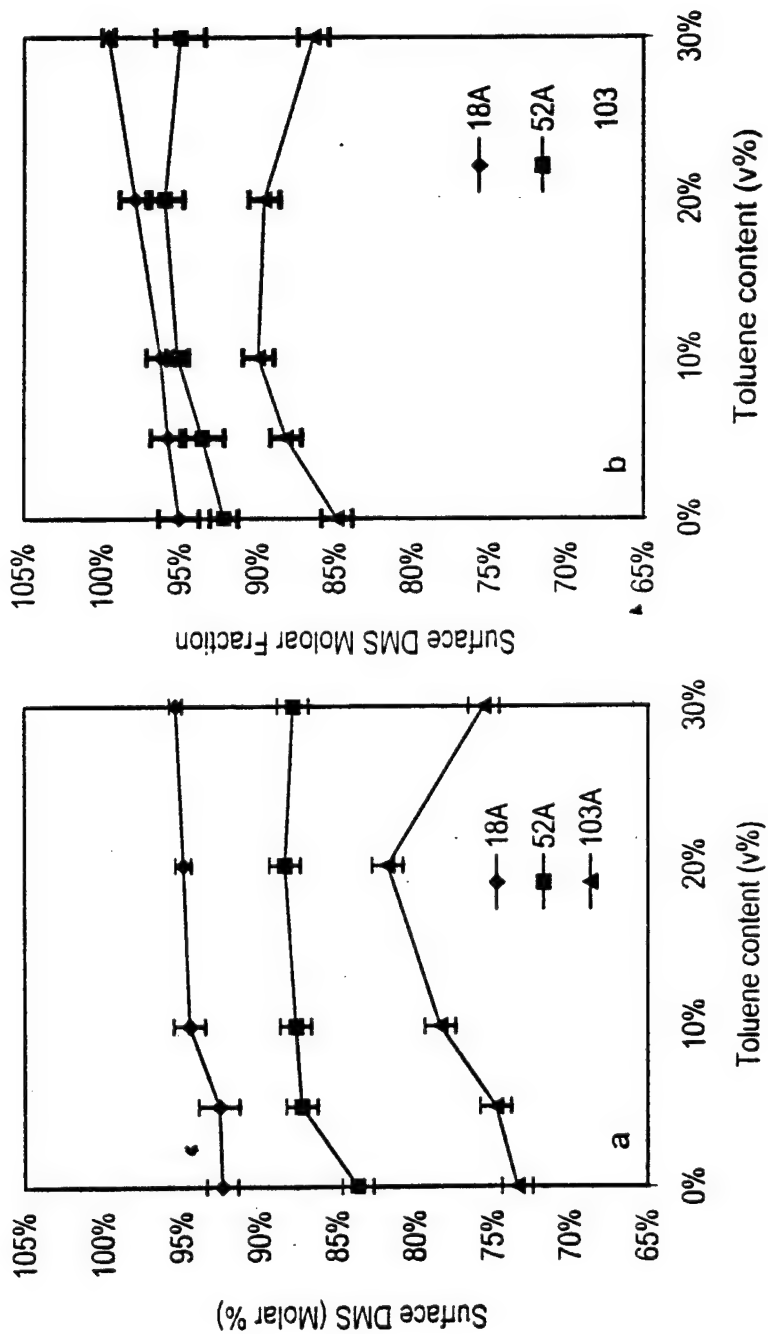


Figure 5a Surface DMS vs toluene content, 1% bulk DMS

Figure 5b Surface DMS vs toluene content, 2% bulk

fig.xls fig5g

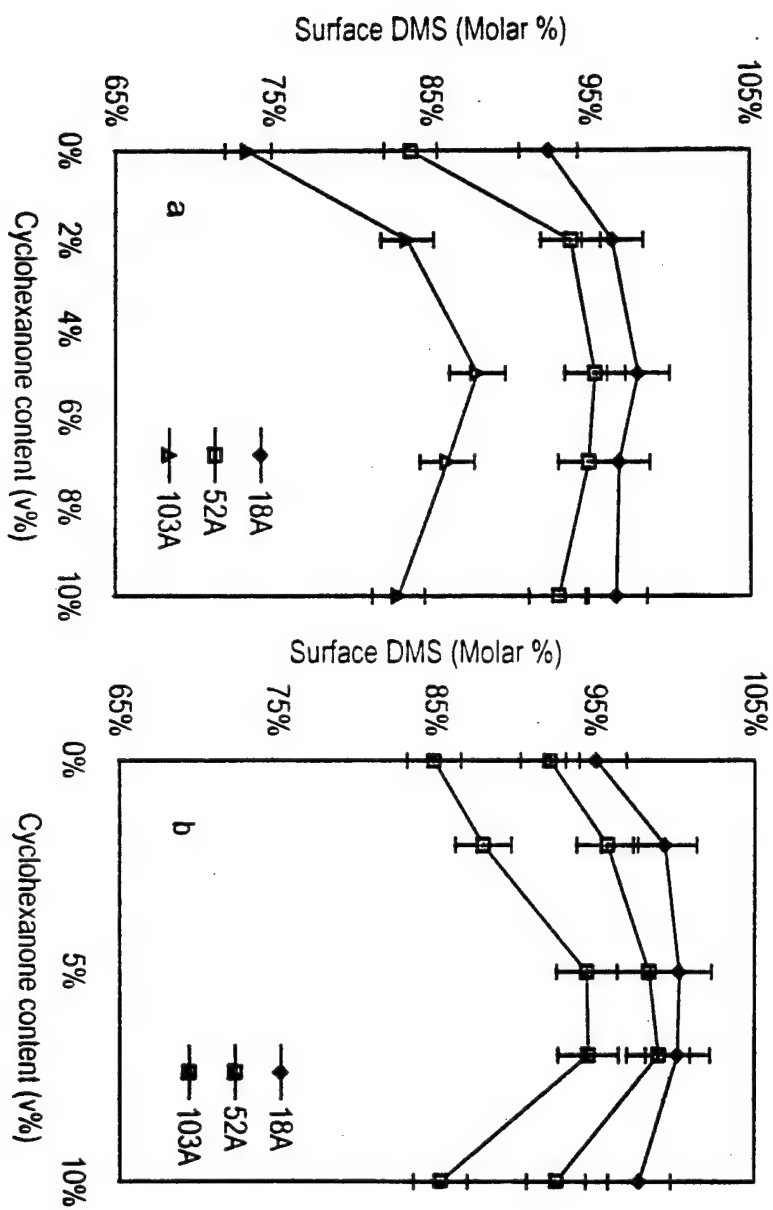


Figure 5a Surface DMS vs cyclohexanone content, 1% bulk DMS

Figure 5b Surface DMS vs cyclohexanone content, 2% bulk DMS

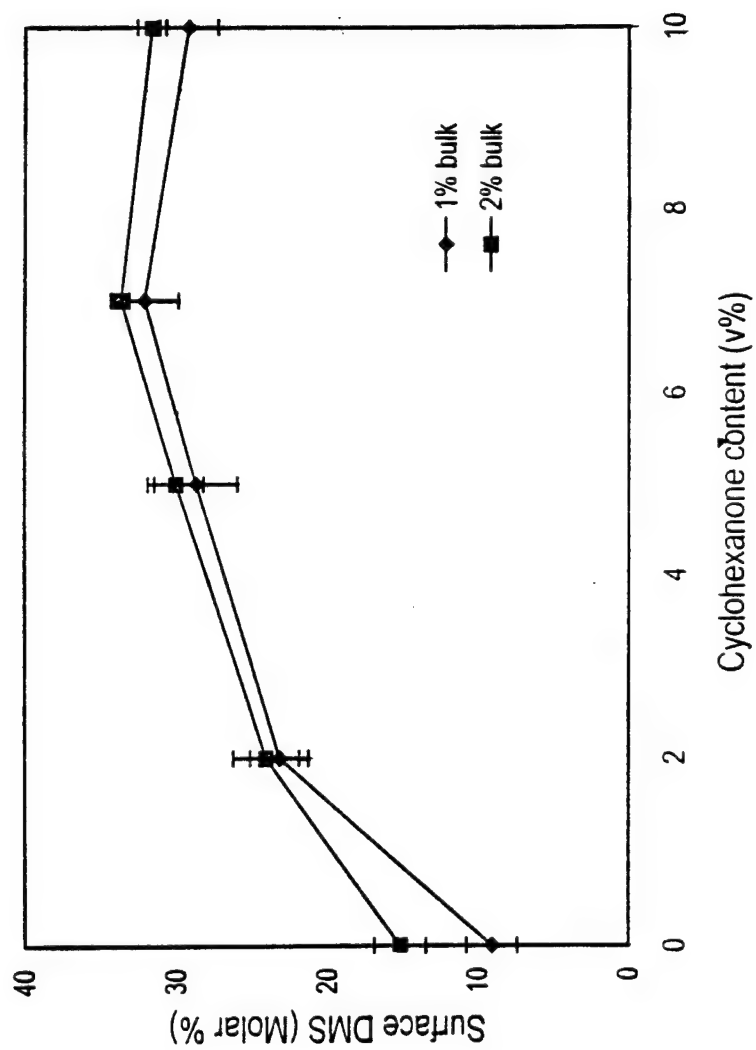


Figure 7 Surface DMS content vs cyclohexanone content in casting solvent, by ATR FTIR at 0.7  $\mu$ m

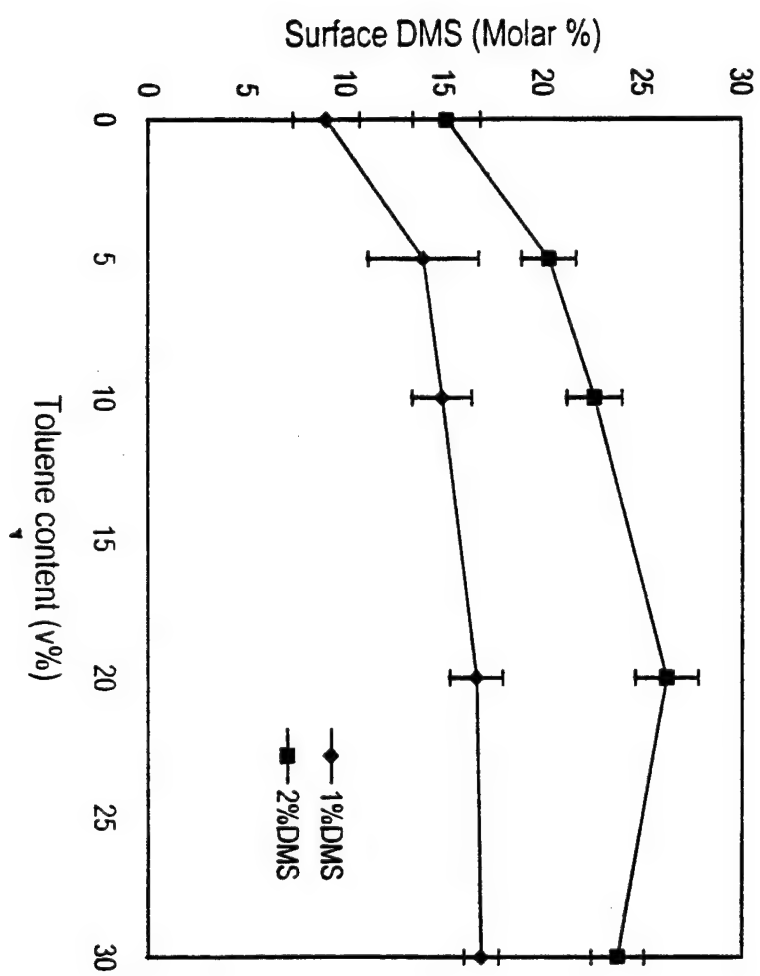


Figure8 Surface DMS content vs Toluene content in casting solvent, by ATR-FTIR analysis

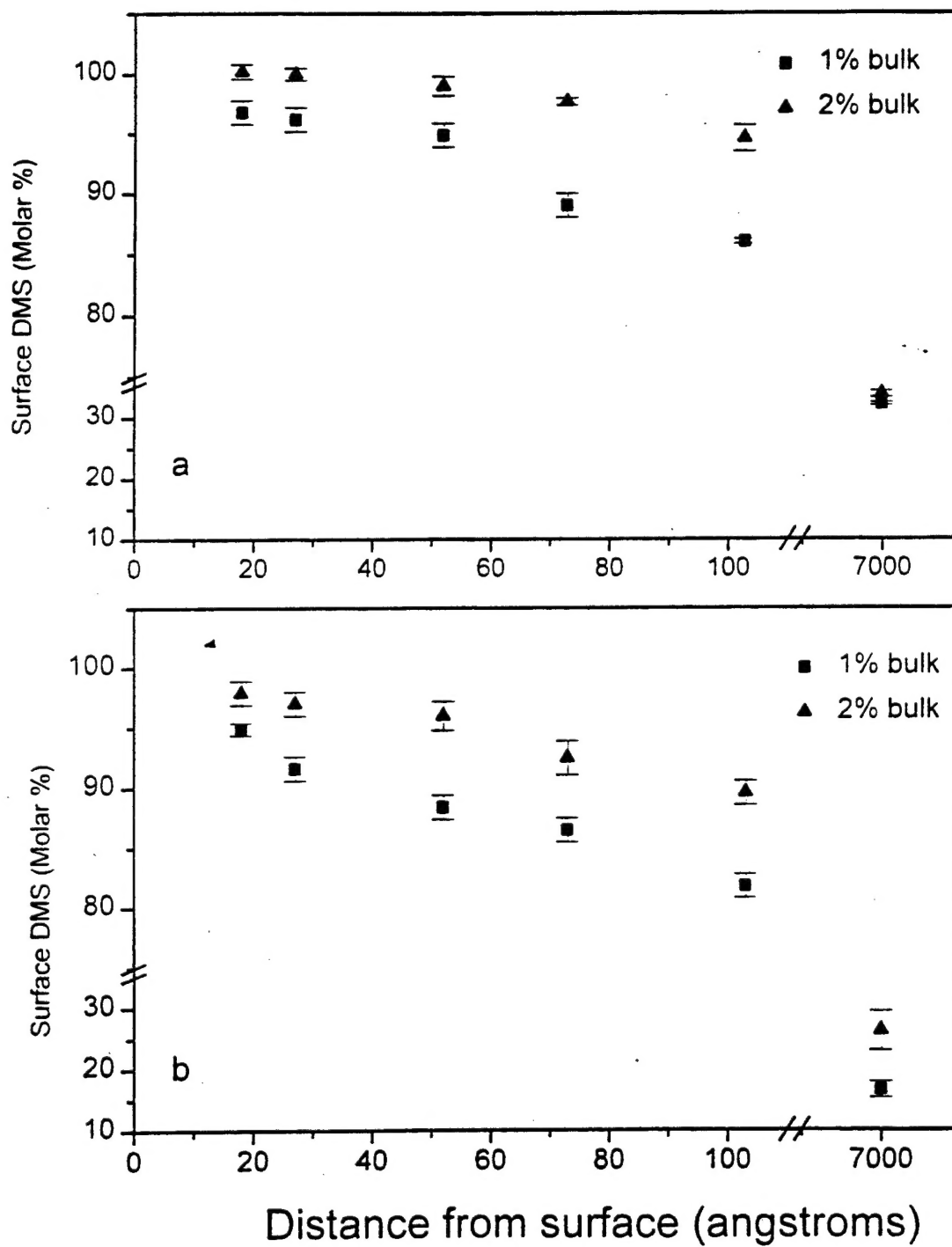
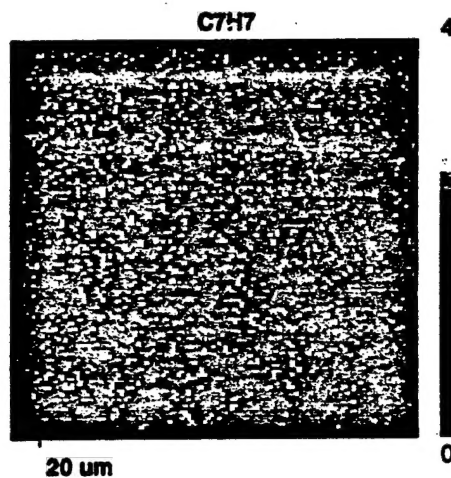
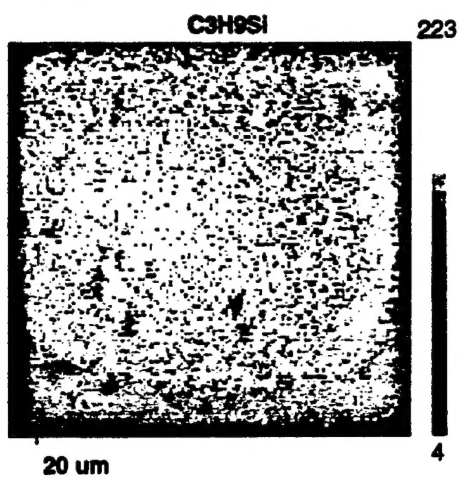
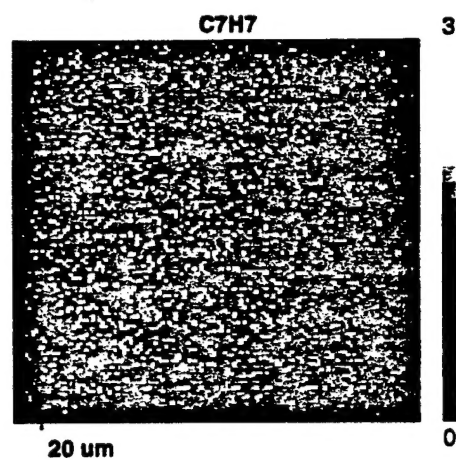
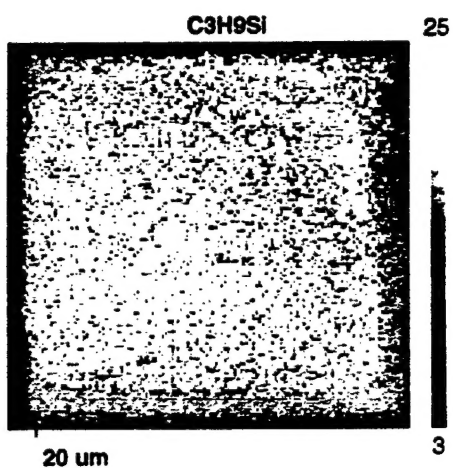


Figure 9 Depth gradient of surface DMS distribution: a sample cast from 7% cyclohexanone in chloroform.  
 b sample cast from 20% toluene in chloroform

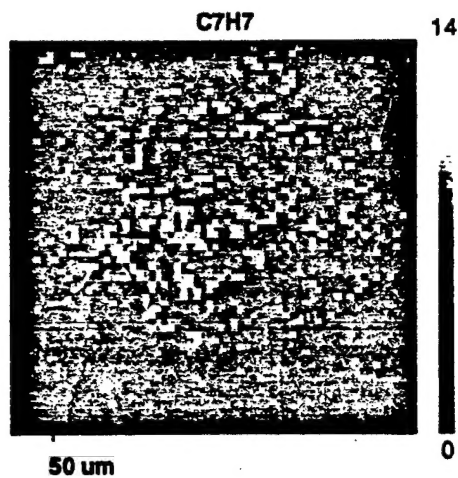
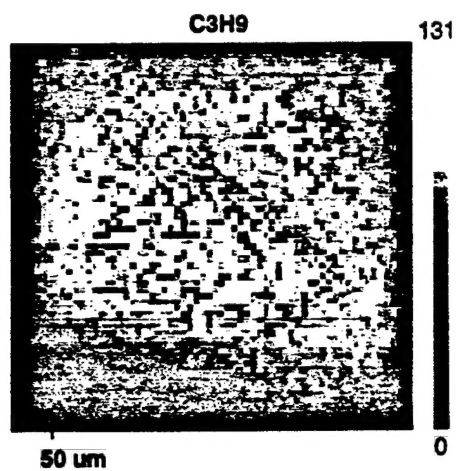
Cyclohexanone/Chloroform cast



Toluene/Chloroform cast



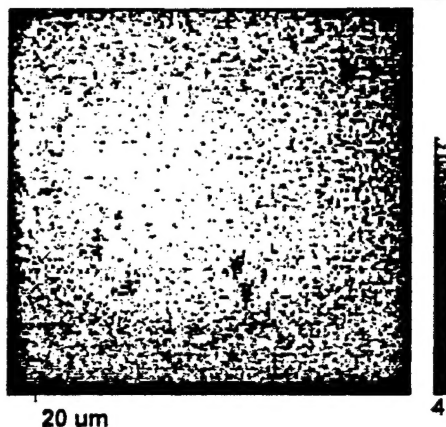
Pure Chloroform cast



Cyclohexanone/Chloroform cast

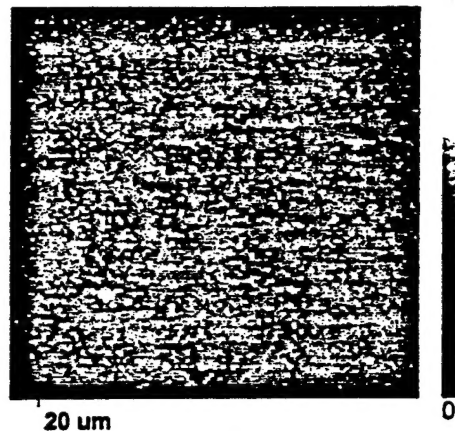
$C_3H_9Si$

223



$C_7H_7$

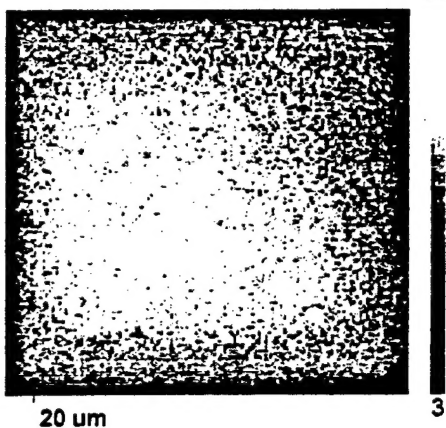
4



Toluene/Chloroform cast

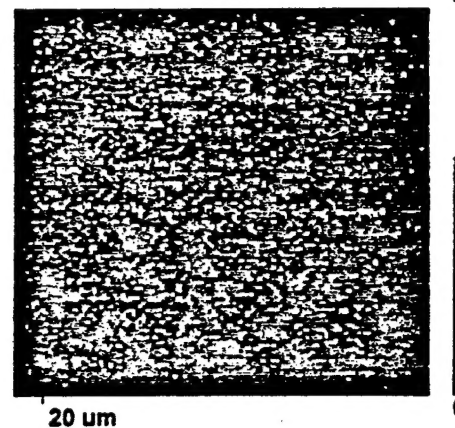
$C_3H_9Si$

25



$C_7H_7$

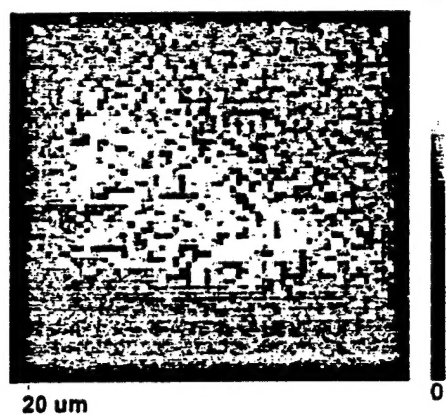
3



Pure Chloroform cast

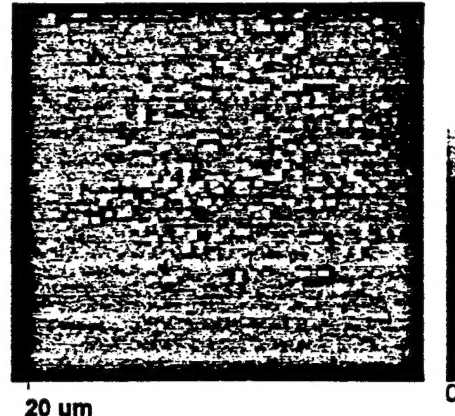
$C_3H_9Si$

131



$C_7H_7$

14



5. ... file #10

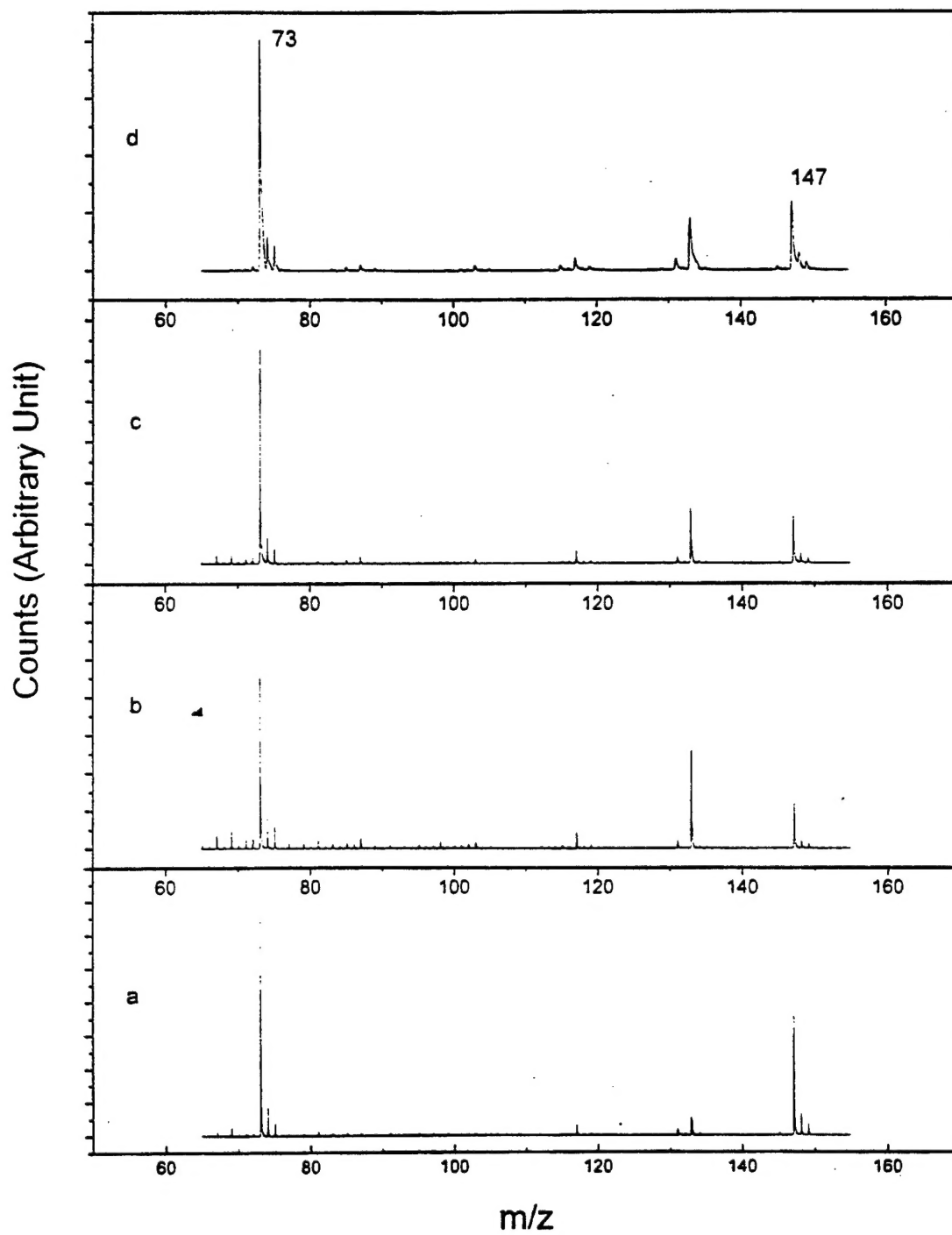


Figure 11